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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
National Risk Management Research Laboratory
Ada, Oklahoma 74820
October 2, 1995

Subsurface Protection &
Remediation Division

MEMORANDUM

SUBJECT: Geochemical/Geohydrologic Report Crystal Chemical Site Vol. 1 Text (July 22, 1994) (GG Report); Assessment of the Technical Impracticability of Ground Water Remediation, Crystal Chemical Superfund Site, Houston, Texas Vol. 1 Report (TI Report) (95-R06-001)

FROM: Scott G. Huling, Environmental Engineer SGH
Applications and Assistance Branch

TO: Lisa Price
Remedial Project Manager (6SF-AT)
US EPA Region 6

The above referenced documents have been reviewed as per the technical assistance request memorandums dated November 30, 1994 and August 10, 1995. The objective of reviewing the GG Report was to become familiar with the hydrogeology of the site prior to the submittal of the TI report. A technical review of this report has been provided and comments are included below.

The objective of reviewing the TI report was to evaluate the technical issues regarding whether the requested TI waiver complies with the intent of the TI guidance. Overall, the report was well written, a good conceptual model of the site was presented, and the TI waiver request appears to comply with the intent of the TI guidance. It is generally recommended that the TI waiver request be approved and further evaluation of alternative remedial strategies be performed. This approval is contingent upon several technical issues related to the TI waiver request in this review. Additionally, there are technical issues regarding the slurry wall should be addressed in the development of alternative strategies.

This review was conducted by Lowell Leach of Dynamac Corp., Dr. Birinder Shergill of ManTech Environmental Research Services Corporation, and me. If you have any questions or would like to discuss any of the comments and recommendations, please call (405) 436-8610.

cc: Rich Steimle, EPA-HQ
Bert Gorrod, EPA-Region VI
Peter Feldman, EPA-HQ
Dr. Birinder Shergill, ManTech Inc.
Lowell Leach, Dynamac Corp.

Geochemical/Geohydrologic Report Crystal Chemical Site Vol. 1 Text (July 22, 1994):

1. This report is very well written and easy to understand. The site investigations thoroughly describe the site geology and hydrology and provide a well detailed history of how arsenic contamination of the site occurred over several years of herbicide manufacturing. It describes how contamination occurred as a result of poor wastewater management in holding ponds and from poor handling of manufacturing chemicals around the site.

2. Detailed investigations, following EPA's issuance of the Record of Decision in 1990, has resulted in an extremely well documented delineation of the contaminated zones and their relationship to the hydrogeology of the four water bearing zones. Contaminant migration from leaking storage ponds into the two underlying buried paleo-channels, where approximately 90 percent of the arsenic contamination exists, is also well documented.

3. During the geologic/hydrologic investigations in 1993, both cone penetrometry and hollow-stem auger coring were extensively used to develop detailed stratigraphic maps of the two shallow contaminated aquifers. Mud rotary drilling and split-spoon sampling techniques were used to characterize stratigraphy and lack of contamination in the two deeper zones (100 and 300 foot zones). Cone penetrometer data was correlated with hollow-stem auger samples to insure accurate characterization of the strata. These correlations were not presented in the text, however. It would have been helpful for the reviewer to have had the opportunity to study these correlations. Previous experience with cone penetrometer logging indicates that penetrometer logs often correlated poorly with actual cored sediments.

4. Extensive pump tests and slug tests were conducted in the two upper aquifers during 1993. Four analytical methods were used to calculate transmissivity ranges for both pumping and recovery tests. Slug test data were analyzed using three accepted methods. Comparison of these methods has provided an accurate interpretation of the transmissivity of the two aquifers.

5. The geologic/hydrologic interpretations presented in the report appear to be comprehensive and accurate. The two buried paleo-channels are obviously the major contaminated area. The gradients are low in both zones so migration is slow. The two channels appear to be confined and serve as stratigraphic traps, holding contaminants in place as a result of sediment gradation at the ends of the channels.

6. The monitoring well and pumping well screen slot sizes and filter packs appear to be arbitrarily selected. Slot sizes of .01 and .02 inches were selected for monitoring wells and pumping wells, respectively. Filter packs of 20 to 40 and 10 to 20 sieve sands were used in monitoring wells and pump test wells, respectively. These may very well be correctly selected, but proper documentation should be provided for all the well construction components. Well development, purging and telescope drilling were all performed properly.

7. This document presents a summary of data and information collected representing a thorough site investigation. The geologic/hydrologic regime and contaminant delineation has been accurately documented. It is recommended that an additional evaluation/investigation of sediments in the ends of the two buried channels is conducted to confirm contaminants cannot migrate from the site, and will remain trapped, i.e. in the two channel sand zones due to gradational changes near the ends of the buried channel.

8. The pumping tests and geologic investigations confirm that the nature of the splay sediments outside of the two channels has a low permeability, substantiating that it would be technically impractical to implement an extraction and treatment system for remediation outside of the two channel zones.

9. There were several errors in the text noted during the review. These are not critical, but it is suggested that corrections be made in the report for technical and editorial clarity:

- Page 11, The second paragraph indicates MW-15 adjacent to Pond # 2 contained 161,000 ppb total arsenic. Figure 1-3 shows this is Pond # 3.

- Page 74, Section 2.10.2. The author needs to define the term "engineered monofill."

- Page 105, last paragraph indicates MW-31 identifies the southern boundary of the arsenic plume. MW-30 is located farther south and contains 40,000 ppb As. MW-33 has a low concentration of As and is located even farther south so it should indicate the southern limits.

- Page 174, Wells discussed in this section are very difficult to locate on maps. They should be shown on Figures 3-5 and 3-6.

- Page 177, The 100 foot zone is described as being unconfined. This is contradictory to earlier statements where this zone is described as a confining impermeable clay zone ranging from 29 to 60 feet in thickness and extending continuously beneath the site.

- Page 72, The next to the last paragraph reads, "water levels were also recorded in wells MW-2, MW-15 and MW-15 using the Stevens Recorders." One of these wells is obviously in error.

- Page 29, There is an obvious error in Table 2-1. P-5 total depth is indicated to be 24.0 feet, while the screened interval was 11 to 27 feet.

- Page 191, The first paragraph indicates the highest arsenic concentration is beneath Pond # 2, but Figure 5-1 contours indicate the maximum concentration is directly beneath Pond # 3. This error appears again in the last paragraph. The concentration of 112 mg/l should be beneath Pond # 3.

- Page 194, There is a misspelled word in the sixth line of the page; "sampling evens" should read sampling events. The seventh line needs editing. It should read -- Table 5-3 shows arsenic concentrations are consistent and unchanging in all five wells over the last decade.

- Page 199, Next to the last paragraph contains a typographical error. 100,00 should read 100,000.

- Page 202, Section 5.6, The last sentence describes three saturated zones (35 ft., 100 ft. and 200 ft.). There is no 200 foot zone. This zone should be 300 feet.

Assessment of the Technical Impracticability of Ground Water Remediation, Crystal Chemical Superfund Site, Houston, Texas Vol. 1 Report:

1.1.3 - Summary of Factors Affecting Ground-Water Restoration

1. (pg. 5) It is generally true that contaminants will diffuse into dead-end pores and present difficulty in recovering these compounds using a pump and treat system. It is unclear what role this process has at this site since it has not been quantified. A more definitive limitation of pump and treat lies with the fact that arsenic has had a long period of time and a high concentration gradient to diffuse into the low permeable clay and silt units. These units have been characterized at this site and their role is likely to be significant.

2. (pg. 5) It is agreed that treatment technologies

generally cannot achieve a treatment efficiency of 99.99%, especially in-situ. However, the areal extent of arsenic contamination at 100,000 µg/L is limited relative to the arsenic concentration > 50 µg/L and therefore, 99.99% treatment efficiency is not required over the entire site.

4.3.1.1 - Gradients and Flow of Ground Water

1. It is logical that the ground water flow in the 35' zone is strongly influenced from the 15' zone, i.e. vertical gradients. Assuming a slurry wall is constructed, it is unclear whether the resulting ground water flow direction and velocity would strongly influence arsenic transport in the southern portion of the site, i.e. where a TI waiver is not being sought. It is recommended to evaluate this issue further.

2. Construction of the slury wall will change ground water flow directions and gradients in the areas outside (and inside) the slurry wall. Specifically, the hydraulic disruption may change the water table level and low lying areas may become saturated, i.e. development of seepage faces which drain the ground water. It is recommended to evaluate the hydrologic impact of the proposed slurry wall on the surface water /ground water interactions.

4.5 Regional Uses of Ground Water

Table 5 indicates that on-site well WSW-1 is contaminated with 750 - 3600 ppb arsenic and the well is screened over 287-307' bgs. Earlier in the report, it was concluded that the 300' water bearing unit was not impacted from waste management activities occurring at the surface. It is unclear how this conclusion can be made given the compromising data in Table 5. This issue should be resolved before a final decision is made regarding the technical impracticability waiver.

4.6.2 - Arsenic Compounds Present at the Site

The TI report indicates that arsenic speciation data for the past two years is questionable. The reason for this error has not been fully explained. Accurate information on arsenic speciation outside the TI zone may be helpful in evaluating the effectiveness of pump and treat and its relation to desorption of arsenic from sediments. It is recommended to evaluate the redox potential and pH, dissolved oxygen, and iron species in the extraction well south of the slurry wall (in the vicinity of MW-30). This information may be used to infer the dominant arsenic aqueous species using Eh-pH diagrams. Sorption or coprecipitation of arsenate species with iron could control arsenic concentrations in ground water. The slurry wall will change the ground water flow patterns in the area south of the slurry wall. This may result in change of redox conditions, arsenic speciation, and desorption rates of arsenic from the sediments. These changes may also result in the revision of estimated time required in remediating the area south of the slurry wall.

4.7 Geochemical Laboratory Studies

(Appendix C - Adsorption Models) It is generally agreed that the time required to clean-up the contaminated sediments will take longer than 30 years. This is the most important conclusion made in this section. However, there are numerous technical issues regarding the approach, calculations, and assumptions used in arriving at this conclusion. Even if these issues were resolved, it is unlikely that the conclusions of the report would not change. Therefore, these comments are not included in this technical review.

5.6 Summary of Hydraulic Models

1. Extensive modeling was done to provide some reasonable indication of the expected behavior of the ROD-mandated pump and treat system. A ground water flow model for the site was developed using MODFLOW. It was not mentioned if a sensitivity analysis was used to quantify the uncertainty in the calibrated model due to uncertainties associated with estimates of aquifer parameters and boundary conditions. It appears unlikely that this would result in a reversal of the major conclusions of the report. However, for technical completeness, it is recommended to address this issue.

2. Comparison of potentiometric surfaces for the 15-ft zone during April 1994 (fig. 21) and September 14, 1994 (fig 34.) indicate different flow patterns. The difference may be due to reversal of ground water flow near the flood control channel. The influence of seasonal variations and effect of water level in the flood control channel on ground water flow in the 15-ft zone should be evaluated, particularly with respect to the proposed slurry wall.

6.4.1 Sensitivity of the PUMP Model to Changes in Kd, Mass Transfer Rates, and Flow Rates

(pg. 86) It was first reported on pg. 74 then on pg. 86 that injecting clean water will not enhance the rate of arsenic removal because the rate of transfer of arsenic from soil to water is diffusion limited, and is independent of the rate of ground water flow. It should be noted that Ficks First Law simply states,

$$F = -D\ dC/dx$$

where F is the mass flux, D is the diffusion coefficient, and dC/dx is the concentration gradient. While it may be true that injecting clean water (or simply pumping faster) will increase ground water flow velocity and push arsenic desorption farther from equilibrium; it should be noted that injecting clean water will increase the rate of diffusion by increasing dC/dx, and F increases linearly.

Similar to the previous comment, assuming this issue were resolved by simulating a "clean water" injection scenario, it is unlikely that the conclusion regarding excessive clean-up timeframes would change. This comment is provided only for technical clarification. However, additional effects of diffusion under the proposed containment scenario are discussed further, below.

7.0 Evaluation of Alternative Remedial Strategies

If pump-and-treat remediation could not be attained, one of the remediation alternatives suggested in the contingency measures of the ROD is containment of the arsenic by installing a slurry wall around the site. Given the circumstances of technical impracticability and the evaluation of the various alternatives considered in this document, it appears appropriate to further evaluate construction of a slurry wall around the site which encompasses the portion of the plume greater than 0.05 mg/L and to the bottom of the 35' zone. This alternative appears to be cost effective and logical.

7.1 Physical Containment

One concern that has not been considered are the effects of diffusion. Diffusion would be of greater concern in the slurry wall scenario rather than the sheet piling scenario. This issue is described in more detail below, in Attachment A.

8.3 Evaluation of Slurry Wall

1. For optimum cost and slurry wall placement, it was proposed to install one extraction well outside of the downgradient end of the wall in the more transmissive buried 35-foot channel to capture a small portion of the arsenic where concentrations are greater than 0.05 mg/L. This scenario, with interior and exterior pumping, appears appropriate and should be further evaluated. The costs and advantages and disadvantages of capping the entire area inside the slurry wall should be compared with the cost of constructing and operating the pressure relief well.

2. Comparison of the areal extent of the TI zone (fig. 7) and the location of a proposed slurry wall (fig. 59) indicates that the slurry wall does not contain the extreme east and west areas of the 15-ft sand TI zone. It is recommended that this issue is clarified.

3. In the eastern area, outside of the proposed wall, it appears arsenic will be enclosed in a stratigraphic trap with the western movement blocked by the slurry wall and on other sides by the low permeability clay that surrounds the 15-foot channel. In the western area it is possible that the construction of the slurry wall will isolate it from high arsenic concentrations near Pond 2. Assuming that these areas are left outside the slurry wall, monitoring of both the eastern and western extremes of the TI zone outside the slurry wall is recommended. This will help in evaluating the transient concentrations of arsenic over time.

General Comments:

1. The TI report presents detailed information and appears to address the TI evaluation components as outlined in the EPA guidance document on TI (U.S. EPA 1993). The geologic, hydrologic, and contaminant information has been obtained by a thorough site investigation as required in the recommended guidelines for evaluating a TI waiver request.

2. The data and information presented and projections made in these reports appear to be reasonable and support the conclusion that pump and treat technology is technically impracticable as a remediation strategy for this site. Since the Administrative Order of Consent for "front-end" waivers has been documented as acceptable, it appears appropriate to accept the requested Technical Impracticability Waiver and develop alternative remedial strategies. There are several technical issues identified above that should be addressed during the continued development of the remedial strategies.

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Attachment A - Arsenic Diffusion Through Slurry Wall Time Estimate

Objective: The objective of this analysis was to calculate the timeframe for significant arsenic concentrations to occur outside of the slurry wall based on an estimate of the interior concentration. Currently, it is unclear whether performance information regarding diffusion limitations is available from other sites, or if other methods of analysis are available. This evaluation was performed in an effort to obtain information on the performance of such systems.

This evaluation is considered a first cut at calculating the time for significant concentrations to occur outside the slurry wall due to diffusion. The assumptions have been identified, and the values used in the calculations have been referenced when possible.

Approach: Assuming the slurry wall scenario is implemented, the timeframe will be estimated for arsenic transport by diffusion from the inside of the slurry wall at equilibrium concentration to the exterior of the slurry wall, reaching the clean-up concentration goal of 50 µg/L using a 1-dimensional diffusion model. This will provide some information on the limitation of the slurry wall containment option that has been selected.

Assumptions: This analysis assumes (1) non-steady state diffusion (2) no advection, (3) retardation, (4) equilibrium aqueous arsenic concentration based on the mass and water volume reported in the TI report (pg. 41), (5) no reaction terms, and (6) aqueous phase only (arsenic associated with solid and non-aqueous phases were not included).

It is reported on Pg. 41 of the TI report that approximately 18,300 lbs of arsenic exists in the 15' and 35' zones, and that these two zones also contain approximately 6 - 8 million gallons of water. The average arsenic concentration assuming all the various concentrations reached equilibrium concentration is approximately 6900 µg/L. This assumption is somewhat arbitrary since it completely ignores the mass of arsenic associated with the solid phase material.

Given:

1. Slurry wall thickness - 3' (assumed)
2. Single phase (aqueous) no porous media present, the rate would be faster with porous media present
3. No advection (horizontal, vertical)
4. Retardation factor (R) = 10.8 - 84 (depending on K_d)
   $R = 1 + K_d(\rho/\eta)$
   K_d = 3.6 ml/g (this avg. value from lab studies was reported to be high relative to calculated field values, TI report, App. C, pg. C-7)

K_d = 0.018 - 1.5 ml/g, avg.+/- s.d.= 0.424 +/- 0.446 (this range of values was reported for field values, TI report, App. C, Table A)

ρ = bulk density of the slurry wall material, 71.7 - 73.4 lb/ft^3 (Baroid Benseal, vendors information on pure sodium bentonite hydrated with water)
η = porosity of the slurry wall material 0.05 (assumed)

5. $[As]_{inside}$, $[As]_{outside}$ = 6900 and 50 µg/L respectively. TI report, Section 4.6.6 (pg.40) estimated 18300 lbs of As, and approx. 6-8X10^6 gallons of water combined in the 15' and 35' intervals = 6900 µg/L.

6. Arsenic diffusivity = 3.7X10^{-5} cm^2/s calculated using the Stokes/Einstein equation (Welty, Wicks, and Wilson 1984)
   D = (KT)/(6πrμ)
   K = Boltzmans constant = 1.38X10^{-16} (ergs)
   T = temperature (K°) assume to be 293°
   r = ionic radius of arsenic = 0.58 (angstroms) As^{+3}; 0.34-0.46 (angstroms) As^{+5} (CRC, 1996)
   μ = viscosity of water @ 20°C = 1 (centipoise)

The effective diffusivity (D*) in porous media is not equal to the free water diffusivity (D). The effect of tortuosity due to solids must be taken into consideration, as indicated in the following equation (eqn. 3.45, Freeze and Cherry, 1979),

$$D^* = \omega D$$

The factor which accounts for tortuosity (ω) ranges from 0.01-0.5. Therefore, the value of D is multiplied by .01-0.5 to get the effective diffusivity in porous media. Assuming ω = 0.1, D* = 3.7X10^{-4} cm^2/s.

Equation: The equation used to describe the idealized diffusional process is also taken from Freeze and Cherry, 1979, equation 9.5. Since it is assumed that there is no advection and that retardation does occur, equation 9.5 reduces to the following:

$$C(x)/Co = \mathrm{erfc}[x/(4\ D^*\ t/R)^{1/2}]$$

where;
C(x) - Arsenic concentration outside = 50 (µg/L)
Co - Arsenic concentration inside = 6900 (µg/L), 69000 (µg/L) was also used to evaluate the diffusion time under high concentrations
erfc - complimentary error function, erfc(x) = 1 - erf(x) erfc and erf function values are found tabular form
x - horizontal distance through the slurry wall = 3 (ft)
D*- effective diffusivity 3.7X10^{-4} (cm^2/s), diffusivity (D) will also be used 3.7X10^{-5} (cm^2/s)

t - time (years)
R - retardation factor = 10.8 - 84 (unitless)

Several conversion factors are needed to assure compatible dimensions.

Results: The time for arsenic to diffuse from inside the slurry wall to the exterior at sufficient concentration and exceed the cleanup standard of 50 (µg/L) has been calculated and is presented in Table 1.

Table 1 - Diffusion Time Estimates

$[As]_{inside}$ (µg/L)	Time (years)	
	R = 10.8	R = 84
Diffusion (D = $3.7X10^{-5}$ cm^2/s)		
$[As]_{inside}$ (µg/L)		
6900	5.3	41
69000	3.4	26.4
Effective Diffusion (D* = $3.7X10^{-4}$ (cm^2/s)		
6900	53	410
69000	34	264

Discussion: The estimated time it takes for arsenic to diffuse through the slurry wall ranges over a wide timeframe. The data in Table 1 raises a concern that arsenic concentrations may diffuse from the slurry wall within a relatively short timeframe. These estimates are not provided with reported confidence intervals because an uncertainty analysis has not been conducted. This is due to the fact that the variability of the parameters involved are not known at this time. However, a better estimate of the timeframe and the uncertainty can be determined when more information is available on the actual values for the arsenic distribution coefficient (K_d) in the bentonite/soil slurry, the tortuosity factor (ω), the concentration inside and outside the slurry wall ($[As]_{inside}$, $[As]_{outside}$), diffusivity (D), porosity and bulk density of the slurry wall (η, ρ), slurry wall thickness (x), etc. Additionally, other factors which were not taken into consideration may also play a significant role;

1. advection,
2. heterogeneities in the slurry wall,
3. arsenic concentrations in the soil,
4. actual mixture of bentonite and native soil, and
5. reactions/behavior of arsenic in the slurry wall.

The unusually high estimate of K_d derived from the laboratory studies may represent an unusually high estimate of the retardation factor. Table 30 of Appendix C indicates that the pH of the slurry was approximately 7.0. At this pH, As^{+5} can become the dominant arsenic specie which would have a significantly greater interaction with the soil than As^{+3}. Therefore, it is reasonable to expect high estimates of Kd. It is believed that the lower estimate of the retardation factor in Table 1 (i.e. average of the field values) more closely estimates the actual field value. However, it is still unclear what interaction will occur between arsenic and the "as-built" slurry wall, i.e. bentonite and native fines. Assuming the diffusion limitation issue is significant in the development of alternative strategies, it is recommended to conduct laboratory studies which evaluate the distribution of arsenic between the slurry material and water at the pH most representative of the ground water at the site. A better estimate of K_d will provide more accurate information on the sorption of arsenic in the slurry wall, and therefore, better information on which to evaluate diffusion and retardation of arsenic in the slurry wall.

While the model used to estimate the time for arsenic diffusion is simple, it involves conservative assumptions and parameter values. These calculations represent <u>one method</u> to evaluate the diffusion limitation of the proposed slurry wall technology. The estimate of the diffusion time <u>in this attachment</u> should be considered a starting point in such an evaluation. Overall, it is important to understand the limitations of such a system prior to investing the time, energy, and resources in its construction.

It is recommended that a more thorough analysis of diffusion limitations to the proposed slurry wall be conducted. Specifically, this would involve a thorough evaluation of the parameters involved. Additionally, it is recommended to evaluate the use of advection as a means of off-setting diffusion. For example, maintaining an inward hydraulic gradient resulting in a net negative flux of contaminants through the wall to offset the diffusive flux outward, through the wall.

References

CRC <u>Handbook of Chemistry and Physics</u>, 76th edition, 1995-1996.

Freeze and Cherry, 1979, <u>Groundwater</u>, Prentice-Hall Inc. Publishers, 604 pp.

U.S.EPA, 1993 <u>Guidance for Evaluating the Technical Impracticability of Ground-Water Restoration</u> (EPA/540-R-93-080).

Welty, Wicks, and Wilson 1984, <u>Fundamentals of Mass Transfer</u>